

MICROBIAL SULFUR ISOTOPE DEPLETION AND MINERALOGY OF PROSPECT MESA

FORMATION SOIL PIT, DRY VALLEYS, ANTARCTICA. P. D. Cavanagh¹, L. M. Pratt¹, D. L. Bish¹, J. L. Bishop², Y. Peng¹ and P. Englert³, ¹Department of Geological Sciences, Indiana University, Bloomington, IN 47405, pdcavana@indiana.edu, ²SETI Institute (Mountain View, CA), ³University of Hawaii at Mānoa.

Introduction: A soil pit from the Prospect Mesa Formation (PMF) near Wright Valley, Antarctica, was investigated using sequential sulfur extraction, stable isotope analysis, and X-ray diffraction (XRD). The Antarctic Dry Valleys (ADV) have previously been used as a potential Mars analog due to their cold and dry environment. The PMF exhibits a varied stratigraphy with layers ranging from morainal gravel deposits, lodgement till, and fossil-rich marine sediments [1]. Seven samples, from the Pit #1, Core 72 Site in the PMF and collected during a 1979/1980 Antarctic campaign [2], were analyzed. Samples were taken at 2-4 cm intervals from the surface sediment layer down to 12-16 cm in depth (Table 1). These samples have high sulfate and evaporite mineral abundances, and their sulfur isotopic compositions were analyzed to assess the origin of the sulfate and potential sources of depletion of $\delta^{34}\text{S}$. We present a potential depletion process that supports the hypothesis that the sulfate was deposited from atmospheric sources that have experienced microbial interactions.

Table 1. Description of ADV samples analyzed.

Sample ID	Description
JB1087	EG#222 Top 1 cm soil at core #72 site
JB1088	EG#219 0-2 cm material at soil pit, 2 km east of Lake Vanda
JB1089	EG#238 2-4 cm, high salt zone
JB1090	EG#215 4-6 cm, high salt zone
JB1091	EG#216 6-8 cm depth
JB1092	EG#217 8-12 cm depth
JB1093	EG#218 12-16 cm depth

Methods: The samples were prepared for sulfur extraction by dry grinding using an agate pestle and mortar. No other preparation procedures were performed.

X-ray diffraction. Prior to sequential sulfur extraction, samples were analyzed using a Bruker AXS D8 Advance X-ray diffractometer (Cu K α radiation) to determine mineralogy. XRD was also used to analyze the samples after each sulfur extraction step. Each sample was measured from 2° to $70^\circ 2\theta$, counting for 2 s. each 0.02° . XRD patterns were evaluated using Bruker's EVA® software, and quantitative phase abun-

dances were obtained via Rietveld refinement with the Bruker TOPAS® software.

Sequential sulfur extraction. Sequential sulfur extraction was performed on the samples based on previous laboratory methods [3-4] in the following five steps:

1. Elemental and organic sulfur extraction
2. Water-soluble sulfate (WSS)
3. Acid-volatile sulfide (AVS)
4. Acid-soluble sulfate (ASSO₄)
5. Chromium-reduced sulfide (CRS)

Elemental sulfur extraction. Samples were measured and transferred onto Whatman® GF/C filter paper inside a glass thimble. The thimble was then fitted at the bottom with a glass flask filled with granular Cu and ~60-70 mL of dichloromethane (DCM). The round-bottom collection flasks were positioned on top of heating mantles and the DCM solvent was then circulated through the system via a condensing tube and dripped onto the sample. The system ran for 24 hours.

Water-soluble sulfate. The extraction of water-soluble sulfate (WSS) was completed by placing ~10 g of sample into individual centrifuge tubes. Approximately 45 mL of milli-Q water was added to each vial and the vials were placed in an orbital shaker for multiple days. These vials were then centrifuged at 5000 RPM for 15 min. The separated liquid was then poured off and filtered with a 0.2 μm filter. The filtered solution was then mixed with 2 M HCl and BaCl₂ to precipitate BaSO₄. The process was repeated until BaSO₄ no longer precipitated, typically for 24 hours. The excess water was suctioned out of the beakers and transferred to new centrifuge vials. BaSO₄ was then repeatedly rinsed (3X), centrifuged, and suctioned, and the precipitates were then placed in an oven at 60°C overnight.

Acid-volatile sulfur. Acid-volatile sulfur (AVS) was extracted following the procedure described by [3]. No detectable AVS (in the form of Ag₂S) was retrieved from the extractions.

Chromium-reduced sulfide. The CRS extraction was modeled after the method presented in [4]. The method is particularly useful in extracting reduced mono-sulfide phases, while leaving other sulfur species

unaltered. Only a trace amount of Ag_2S precipitated from all samples, and quantitative and isotopic measurements could therefore not be completed.

S isotope analysis ($\delta^{34}\text{S}$). The water-soluble sulfate in the precipitated BaSO_4 was the only sulfur yield that could be recovered and analyzed for sulfur isotopic composition. Between 0.36 and 0.44 mg of BaSO_4 was mixed with 1 to 2 mg of V_2O_5 in a tin capsule. Sulfur isotope ratios in the BaSO_4 were measured using a Costech ECS4010 elemental analyzer coupled to a Delta V Advantage isotope ratio mass spectrometer. The isotope data are presented with respect to the VCDT (Vienna Cañon Diablo Troilite) reference scale. Analytical reproducibility was better than $\pm 0.3\text{\textperthousand}$ for standards and duplicate samples.

Results: All samples contained a significant amount of water-soluble sulfate, with some samples requiring six leaches to fully dissolve all of the sulfate. The sequential sulfur extraction yielded mostly water-soluble sulfate through the leaching process. Yields were detected, but not quantitatively recoverable for chromium-reduced sulfide extraction steps. Yields were not detected for the acid-soluble sulfate or acid-volatile sulfide steps.

Table 2. Quantitative XRD results.

Mineral	JB1088 (wt% crystalline)	JB1089 (wt% crystalline)
Plagioclase (An65)	33	14
Halite	-	27
Quartz	27	17
Orthoclase	12	-
Chabazite	5	5
Dolomite	5	1*
Glauberite	3	2
Gypsum	3	2
Hornblende	2	1*
Biotite	2	-
Kaolinite	2	2
Anhydrite	0.2*	0.7*
Blödite	-	8
Microcline	-	15
Calcite	-	2

- Not detected, * At or near detection limits

Mineralogy. XRD analysis showed that the samples consist of major pyroxenes, feldspars, and quartz as in previous studies [e.g. 7,8]. Minor phases include sulfates, clays, and zeolites. Halite represents a large proportion of some of the samples (as much as 26%). Water-soluble sulfate minerals gypsum and glauberite ($\text{Na}_2\text{Ca}(\text{SO}_4)_2$) were detected (~2-3 wt%). Subsequent XRD analysis after the initial WSS leaching demonstrated that the sulfates were removed; the peaks for gypsum and glauberite vanished. Rietveld analysis was performed to obtain more detailed mineralogical information for two samples (Table 2).

Sulfur isotopes. Isotopic analysis of each of the leachates revealed a depletion from $\sim 21\text{\textperthousand}$ (value for ocean sulfate) to $\sim 17\text{\textperthousand}$ in the top layers (JB1087 / JB1088). Lower depth samples were consistently $\sim 15\text{-}16\text{\textperthousand}$.

Discussion: The depletion in ^{34}S rules out purely oceanic to atmospheric transfer mechanisms. An intermediary mechanism must be contributing to the depletion in ^{34}S . We propose that the DMSP/DMS pathway (Fig. 2) is partially responsible for the depletion in ^{34}S compared with that of ocean sulfate. In this scenario, seawater sulfate is initially taken up by macroalgae, reduced, and used to synthesize dimethylsulfoniopropionate (DMSP).

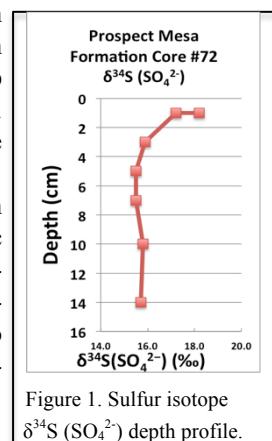


Figure 1. Sulfur isotope $\delta^{34}\text{S}(\text{SO}_4^{2-})$ depth profile.

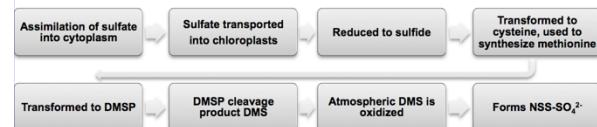


Figure 2. DMSP/DMS formation of non-seawater sulfate [5].

This pathway ultimately synthesizes dimethylsulfide (DMS), which is released into the atmosphere and oxidized into non-seawater sulfate [5]. The DMSP/DMS process has been shown to account for a depletion from $\sim 21\text{\textperthousand}$ to $\sim 17\text{-}19\text{\textperthousand}$ in DMSP and in subsequent degradation products DMS and NSS- SO_4^{2-} [5]. High concentrations of DMSP and DMS have been documented in the Antarctic and can be correlated to algal blooms [6]. The DMSP/DMS process does not fully account for an additional depletion in ^{34}S shown at lower depths.

Conclusions: Preliminary analysis of the PMF sediments is consistent with previously observed depletion of ^{34}S in sediment from the Antarctic Dry Valleys compared to marine sulfate in the Antarctic Ocean. Our data are consistent with a microbial process in which volatile products from marine algae, such as DMSP and DMS, may be responsible for the observed depletion in ^{34}S with sulfur oxidized and transferred via atmospheric processes.

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References: [1] S.A. Arcone & A.J. Delaney (2000), SPIE, 4084, 772-777. [2] E. Gibson et al. (1983), JGR, 88(S02), A912. [3] Zaback & Pratt (1992), Geochim. Cosm. Acta, v56, 763-774. [4] Canfield et al. (1986), Chemical Geology, v54, 149-155. [5] Oduro et al. (2012) PNAS, 109(23), 9012-9016. [6] J.A.E. Gibson et al. (1990) Marine Biology, 104, 339-346. [7] Bishop et al. (1996) GCA, 60, 765-785. [8] Bishop et al. (2014) Phil. Trans. R. Soc. A 372, 20140198.